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The Complex Interaction between Marine Debris and Toxic Chemicals in the Ocean

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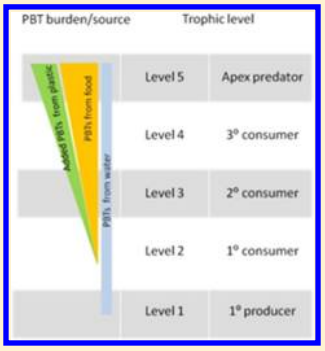
ABSTRACT: Marine debris, especially plastic debris, is widely recognized as a global environmental problem. There has been substantial research on the impacts of plastic marine debris, such as entanglement and ingestion. These impacts are largely due to the physical presence of plastic debris. In recent years there has been an increasing focus on the impacts of toxic chemicals as they relate to plastic debris. Some plastic debris acts as a source of toxic chemicals: substances that were added to the plastic during manufacturing leach from plastic debris. Plastic debris also acts as a sink for toxic chemicals. Plastic sorbs persistent, bioaccumulative, and toxic substances (PBTs), such as polychlorinated biphenyls (PCBs) and dioxins, from the water or sediment. These PBTs may desorb when the plastic is ingested by any of a variety of marine species. This broad look at the current research suggests that while there is significant uncertainty and complexity in the kinetics and thermodynamics of the interaction, plastic debris appears to act as a vector transferring PBTs from the water to the food web, increasing risk throughout the marine food web, including humans. Because of the extremely long lifetime of plastic and PBTs in the ocean, prevention strategies are vital to minimizing these risks.



INTRODUCTION

Marine debris is any man-made, solid object or material that enters our waterways either directly or indirectly.[1] Marine debris is widely, but unevenly distributed around the globe[2−8] and may be organic (wood, paper, natural fibers, plastics) or inorganic (metal, glass, ceramics, concrete), with much of the marine debris being plastic.[4,5] Marine debris leads to a variety of adverse impacts, including stranding on shore, entanglement, "ghost fishing", direct injury to humans or wildlife, physical damage to watercraft, and ingestion by marine life leading to blockage of their digestive systems.

Much of the concern for marine debris focuses on plastic debris[3,6] because of their persistence,[2,7,8] their hydrophobic nature, and, in some cases, their tendency to float, allowing them to be transported significant distances.[9] Other types of marine debris raise fewer concerns: Inorganic materials persist in the environment, but are generally not bioavailable (e.g., concrete) or are substantially similar, if not identical, to naturally occurring substances (e.g., glass and sand). Furthermore, inorganic materials are unlikely to float, so are less likely to be transported significant distances. Wood, paper, and natural fibers may float and be transported significant distances, but will degrade via the same mechanism as naturally occurring biomass, so generally will not accumulate. These materials may be unsightly and cause physical impacts, including entanglement, but they are not likely to pose long-term risks. In terms of marine debris, plastic is a special case.

No one is sure how long traditional plastics persist in the environment,[8,10,11] but rates may be as slow as just a few percent of carbon loss over a decade.[2] Plastic objects typically fragment into progressively smaller and more numerous particles without substantial chemical degradation.[4,8,12] Furthermore, although much of the marine debris research focuses on floating plastic debris, it is important to recognize that not all plastic floats. Depending on the density of the material and the presence of entrapped air, marine debris may float or sink.[2] After some amount of time in the ocean, floating plastic debris may become sufficiently fouled with biological growth that it sinks.[13] As a result, plastic debris will be found throughout the water column, but largely concentrated near the surface and on the ocean floor.

The purpose of this review is to examine the current knowledge surrounding plastic marine debris and its interaction with toxic chemicals in the ocean. A better understanding of the state of the science will lead to a better understanding of what can be done to minimize the risk from that interaction as well as inform future avenues of research.

Plastic in Commerce and Municipal Solid Waste. Plastics are extraordinarily valuable materials and are used for myriad applications, including structural materials, packaging, service ware, and toys. In 2008, plastics represented about 12% of the municipal solid waste (MSW) generated in the United States, or about 30 million tons, of which over 94% (by weight) was discarded.[14] In MSW, many plastic objects include a plastic recycling code that identifies the type of plastic. Table 1 shows the amounts of each plastic in MSW, the percentage of the total plastic load in MSW, and the percentage of each type that is recycled. Other plastics, such as nylon (carpet fiber, apparel) and cellulose acetate (cigarette filters) are rarely labeled with

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Table 1. Types of Plastic in U.S. Municipal Solid Waste (MSW) in 2008

plastic code; name and abbreviation of polymer; common uses	millions of tons of plastic in MSW	polymer as a percentage of total plastic MSW	percentage of type recycled
1 – **polyethylene terephthalate** [PET] (soda bottles)	3,740	12	20
2 – **high-density polyethylene** [HDPE] (milk jugs)	5,350	18	11
3 – **poly(vinyl chloride)** [PVC] (pipes, building material, shower curtains)	1,660	6	0
4 – **low-density polyethylene or linear low-density polyethylene** [LDPE/LLDPE] (plastic bags, six-pack rings)	5,880	20	6
5 – **polypropylene** [PP] (reusable food containers, beverage bottle caps)	4,190	14	1
6 – **polystyrene** [PS] (CD crystal cases, service ware, blown foam packaging)	2,620	9	1
7 – **other** all other types, including **polycarbonate** [PC] (reusable beverage bottles, CDs, DVDs), **acrylonitrile-butadiene-styrene** [ABS] (exterior cases for electronic devices), **polylactic acid** [PLA] (sometimes called "corn plastic"), **polyhydroxy alkanoates** [PHA]	6,610	22	0

recycling codes and may not be captured in the totals in Table 1. Plastic is ubiquitous in our economy and, as a result, in our waste. Furthermore, studies have shown that much of plastic marine debris is blown or washed out to sea from land sources.[15]

Predominance of Plastic Debris. Research on the amount and distribution of plastic debris of various sizes is ongoing.[16] A substantial amount of the debris floating at or near the surface is plastic, mostly small plastic fragments.[17−19] Variations in monitoring methods and locations make data, especially beach data, difficult to interpret. Nevertheless, recent research on the distribution of plastic debris in the North Atlantic and North Pacific show "high densities of floating plastic debris, especially... within a few hundred kilometers of the coast and in the gyre centers".[4] It is also notable that, despite continued growth in global plastic production and use, there has been some stabilization of the debris loads in the Atlantic,[20,21] so "efforts to reduce plastic input at a land-based source may be measurably effective".[21] Furthermore, stranding rates of plastics on shorelines showed a considerable, sustained increase throughout the 1980s and 1990s, but stranding may now be stabilizing.[4,9] Recently, more research has focused on plastic debris on the sea floor.[22,23] "Plastics dominate macro-debris [>20 mm] on the sea floor to an extent similar to which they dominate floating litter and beach debris".[4,9] Many types of plastic are denser than seawater (see Table 2) and will tend to settle at or near the point that they enter the water system, but may be transported by underwater currents.[24−26] In general, plastic debris on the sea floor will be less mobile than plastic floating on or near the surface.[23]

Table 2. Common Types of Plastics and Their Densities[a]

polymer type	density (g/mL)[38]	comment
polyolefins		
polypropylene (PP)	0.90	80−90% of floating debris[37]
polyethylene (LDPE, HDPE)	0.92−0.96	5−15% of floating debris[37]
polystyrene (PS)	≤1.05	sometimes expanded to foam (e.g., "styrofoam")
acrylonitrile-butadiene-styrene (ABS)	1.07	
nylon	1.09	
polycarbonate	1.36	
cellulose acetate	1.42	
poly(vinyl chloride) (PVC)	1.4	
polyethylene terephthalate (PET)	1.55	soda bottles; frequently entrap air

[a]Seawater density: approximately 1.02−1.03 g/mL. Note that densities can vary depending on the processing conditions.

Physical Impacts of Plastic Marine Debris. Many of the impacts of marine debris are well documented.[5,22,27] The most visible impacts are the piles of stranded debris along the shoreline and dramatic images of entanglement of various animals, including marine mammals, sea birds, and turtles. Ingestion of debris by a variety of species is common[5,28−33] and may alter wildlife feeding habits or entirely block digestive systems of birds, turtles, or other marine life. Floating debris can also transport invasive species long distances.[4] In addition, "ghost fishing", where derelict fishing gear left at sea continues to capture and kill ocean life, is widely recognized as a problem for many marine species including fish, turtles, mammals, and birds.[27]

Types and Characteristics of Plastic Debris. Nearly every type of commercial plastic is present in marine debris.[31] Assuming that plastics are present in marine debris in roughly the same proportion as they appear in MSW (see Table 1), about half of the plastic (by weight) in marine debris is buoyant enough to float on seawater (density approximately 1.02−1.03 g/mL, depending on temperature and salinity); the rest will sink to the sea floor. It should not be "surprising to find that there are numerous reports of sunken marine debris of all kinds";[27] rather, plastic debris should be expected and is found both near the surface and on the sea floor.[22,26,34−36] Whether plastic persists at intermediate depths is a more complex question requiring further research.

Floating marine debris is dominated by polyethylene (e.g., plastic shopping bags, six-pack rings) and polypropylene (e.g., yogurt containers, soda bottle caps)[24,25,31,37] because of their inherent buoyancy, their broad utility, and high production volumes. Plastics with a density greater than that of seawater (PET, ABS, PVC, PC, etc.) will only float if the object has entrapped air. For example, cellulose acetate is the plastic used in cigarette filters and has a density of approximately 1.42 g/mL[38] so would be expected to sink. However, cigarette filters can entrap air and float until they become saturated with water, at which point they will sink.

Some of the smallest forms of plastic in the ocean are called "microplastics".[16,39] Microplastics arise from the fragmentation of larger pieces as they weather[4] or from surface water, where they are present because of the use of plastic abrasives, especially in personal care products[40−42] or as a result of shedding during laundry.[43] These types of plastic (particles and fibers) may not be removed by standard wastewater treatment processes and pass through treatment facilities largely unchanged.

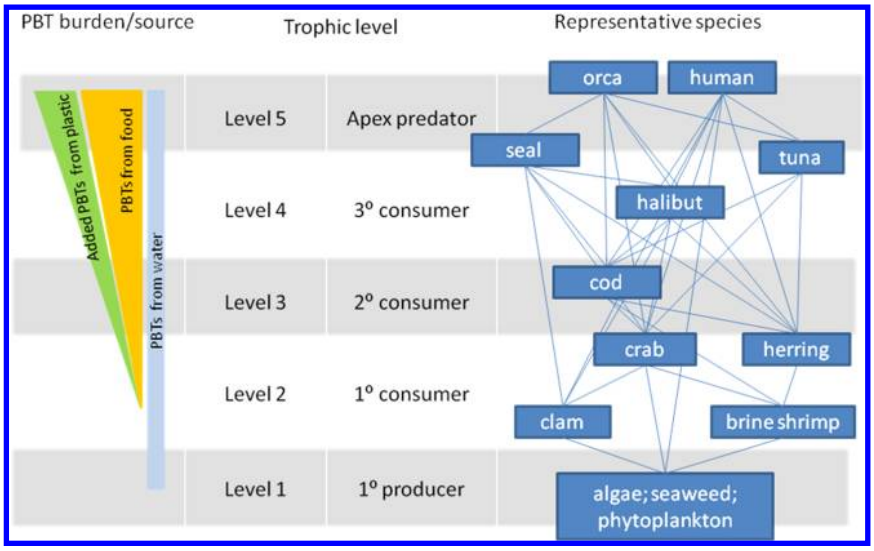

Figure 1. Relationship between trophic level and PBT burden from water, food, and plastic. Trophic level depends on amount and level of food eaten. For example: a crab eats 30% clam (level 2), 30% brine shrimp (level 2), and 40% seaweed (level 1). The crab's trophic level is therefore 2.6 (1 + 0.3 * 2 + 0.3 * 2 + 0.4 * 1).[122] Green "wedge" shown at far left qualitatively represents the portion of PBTs attributable to various species ingesting plastic.

■ PLASTIC DEBRIS AND TOXIC CHEMICALS

Plastic debris throughout the water column may present risks beyond those listed above that result from plastic debris' physical presence. In particular, the relationship between plastic debris and toxic chemicals has been the subject of study in recent years.[2,29,37,44−50] Plastic debris can be a source of toxic chemicals: Some plastics will release toxic chemicals that have been added to enhance the performance of the plastic. Plastic debris may also be a sink for toxic chemicals: toxic chemicals from the environment sorb to the debris, only to be released later.[51,52] In either case, wildlife that ingest plastic are at increased risk for toxic effects and may accumulate toxic chemicals in their bodies to the extent that the pollutants desorb or leach from the plastic. If toxic chemicals accumulate in marine species, they may be transferred up the food chain and into human diets. It is this aspect of toxic chemicals and plastic debris that is especially concerning.

Plastic Debris as a Sink for Toxic Chemicals. Substances that are persistent, bioaccumulative, and toxic (PBTs), such as dichlorodiphenyltrichloroethane (DDT) or polychlorinated biphenyls (PCBs), are of particular concern for human health and the environment.[53] Their properties make them priority pollutants and potential risks to humans and ecosystems. PBTs may enter the environment through dispersive use (e.g., pesticides), industrial releases (e.g., dioxins, polycyclic aromatic hydrocarbons), or release from objects in the environment (e.g., polybrominated diphenyl ethers, PCBs). PBTs resist degradation in the environment, so they can persist for years or even decades. PBTs also accumulate in organisms at a variety of trophic levels (levels in the food web, see Figure 1). Finally, PBTs are toxic to humans and other species. As a result of their properties, PBTs can be especially insidious, even at low levels in the environment, because they can accumulate up the food web, leading to toxic effects at higher trophic levels even though ambient concentrations are well below toxic thresholds. Persistent Organic Pollutants (POPs), a short list of especially persistent, bioaccumulative, and toxic compounds, are a class of PBTs that are relatively well understood and well studied. POPs have been limited, banned, or phased out of commerce in many countries, but some continue to be used, especially in developing countries.[54] POPs include DDT and its degradants, dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), PCBs, polychlorinated dibenzo-*p*-dioxins ("dioxins"), and the structurally similar polychlorinated dibenzofurans (Table 3).

Generally PBTs have very low water solubility (i.e., they are hydrophobic). For this reason, when in the ocean, they tend to partition to sediment or concentrate at the sea surface microlayer.[55−62] When the PBTs encounter plastic debris (also hydrophobic), they tend to sorb to the debris. In fact, polyethylene is used as a sorbent to detect PBTs in aqueous

Table 3. POPs (in Italics)[54] and Examples of other PBTs

Aldrin	pesticide
Chlordane	pesticide
DDT (also DDE, DDD)	pesticide. DDE and DDD are degradants and markers for DDT exposure or release; often are counted as "total DDT" or ∑DDT
Dieldrin	pesticide
Endrin	pesticide
Heptachlor	pesticide
hexachlorobenzene (HCB)	transformer fluid
Mirex	flame retardant and pesticide
polychlorinated biphenyls (PCBs)	transformer fluid and plasticizer
polychlorinated dibenzo-p-dioxins ("dioxins")	industrial and incineration byproduct
polychlorinated dibenzofurans	industrial and incineration byproduct
Toxaphene	pesticide
polybrominated diphenyl ethers (PBDEs)	flame retardants added to plastics and cushioning foam
mercury/methyl merucry	wide variety of uses, also released by burning coal. inorganic mercury is converted to methyl mercury in the environment
polycyclic aromatic hydrocarbons (PAHs) or polycyclic aromatic compounds (PACs)	components in crude oil, byproduct of fossil fuel combustion
perfluorinated alkyl surfactants (PFASs)	oil and stain repellants; semiconductor manufacturing; processing aids

environments, including sediments.[63−68] Different pollutants sorb to different plastics to a variety of degrees as measured by a partition coefficient, K_d, defined as the ratio of q (the mass of the substance sorbed on the plastic in μg substance/kg debris) to C_{sw} (the concentration of the substance in seawater in μg substance/L seawater) as shown in eq 1.[69]

$$K_d = \frac{q}{C_{sw}} \quad (1)$$

The amount of a substance sorbed on the plastic debris (q) will therefore depend on K_d and the concentration of the substance in the local water.[29] Note that Mato et al. showed that PBTs deposit on plastic debris primarily from seawater, not air.[46] Plastic debris on the sea floor may sorb PBTs from the sediment,[23,37] although the transfer may be mediated by seawater. Furthermore, plastic debris sorbs PCBs and DDE about one hundred times better than naturally occurring suspended organic matter.[46]

PCBs and DDE sorb to polyolefin debris with a K_d on the order of 100 000−1 000 000 over seawater.[46] Similarly, phenanthrene, a PAH, partitions to plastic debris 380−13 000-fold over seawater.[69] Weathered plastic polyethylene debris tends to sorb more pollutants than does virgin material, but other plastics do not show statistically significant differences in K_d with weathering.[29,46,69] PBT sorbtion to plastic debris has been suggested as a way to monitor global PBT levels.[51]

Overall, the potential for PBTs to sorb to plastic debris is complex. Because of the variety of PBTs and plastics, their behavior in the environment will vary, but they are more likely than not to preferentially sorb to plastic debris. The particular sorption coefficients will depend on the particular PBT and plastic: polyethylene sorbs PCBs more readily than polypropylene does,[70] but in most cases, and especially in the buoyant plastics, the hydrophobicity of PBT and plastic will generally favor sorption. Furthermore, sorbtion is affected by weathering of plastic, which may change how quickly and how thoroughly PBTs sorb onto the debris, and by biofouling, which may slow the exchange as the plastic surface becomes covered by organisms.[44] Nevertheless, PBTs will, over time, sorb to plastic debris. Generally, the longer plastic is in the water, the higher the concentration of sorbed PBTs. Once sorbed, the fate of the sorbed PBTs will depend on the fate of the plastic debris.

While sorbed on floating plastic debris, PBTs may be transported significant distances.[71] This transportation is in addition to other mechanisms of transportation of PBTs,[72] although the relative contribution of various mechanism is unknown. Floating plastic debris can be transported across an ocean or even to an adjacent ocean.[73] This tendency to transport PBTs globally complicates risk reduction efforts: A country may ban a particular PBT, but still face risk through the food supply if that PBT is released in another country and sorbs to plastic debris in the ocean which then may enter the food web when the plastic is ingested by one of many marine species.

PCBs. Plastic tend to concentrate whatever PBTs occur in the area.[74] For example, because of the historic production and use patterns, debris near the industrial coasts of the U.S. and Japan have higher concentrations of sorbed PCBs than debris in other locations.[31,71,73] Sorbed PCB concentrations vary with the local concentration of PCBs in the water and the plastic's time in the water: it may take months for the PCBs to equilibrate between the water and plastic.[46,63] As shown in Table 4, floating and stranded plastics have been found with sorbed PCB concentrations ranging from 4 to 5000 ppb.[37,46,49,68,70,75,76]

Table 4. Summary of PCB Concentrations on Plastic Marine Debris

material	location sampled	PCB concentration (ppb)	reference
polystyrene	floating New England	up to 5000	75
plastic pellets	floating North Atlantic	300−600	68
plastic pellets	floating/stranded North Pacific	27−980	37
plastic pellets	stranded Japan	<28−2300	70
plastic pieces	ingested by seabirds Southern Brazil	243−491	76
plastic pellets	floating/stranded Japan	4−117	46
plastic pellets	stranded Portugal	46−54	49
plastic pieces	Walpole, Maine	11	23
plastic pieces	floating/stranded North Pacific	1−436	50
plastic pieces	floating North Atlantic	1−29	50

DDT/DDE/DDD. Other PBTs accumulate in plastics as well. Total DDT (represented as ∑DDT, which is the sum of DDT and its degradants, DDD and DDE) was found on plastic particles ingested by seabirds in southern Brazil at concentrations ranging from 64.4 to 87.7 ppb.[76] DDE was found on pellets collected from Japanese coastal sites, ranging from 0.16 to 3.1 ppb.[46] Pellets collected from Portuguese beaches had ∑DDT ranging from 1.9 to 4.5 ppb.[49] Plastic from various sampling sites around the Pacific gave ∑DDT concentrations from 22 to 7100 ppb[37] and 0 to 198 ppb.[50] Pellets collected near the U.S. and Southeast Asia had ∑DDT concentrations from 100 to 300 ppb.[68] Plastic near Vietnam tends to have DDT, rather than its degradants, DDD or DDE, because DDT is still used to control malaria-bearing mosquitoes.[68]

Polycyclic Aromatic Hydrocarbons (PAHs). Unlike other PBTs, polycyclic aromatic hydrocarbons (PAHs) are ubiquitous—they occur naturally as a component of petroleum, and arise from anthropogenic sources, largely as a byproduct of incomplete combustion. Many PAHs are also PBTs; some are likely carcinogens and exhibit developmental toxicity along with other toxic effects.[77] Like other PBTs, PAHs are very hydrophobic and partition from water to sediments and to plastic debris. Rios et al. report plastic pellets with PAH concentrations between 39 and 1200 ppb.[37] The types of PAHs found indicate that fossil fuel combustion is the primary source of the sorbed PAHs, suggesting that PAHs would likely be found sorbed to plastic anywhere around the globe. Another study sampling from various sites around the Pacific and Atlantic found PAH concentrations up to 9297 ppb.[50] In this study, the distribution of PAHs was consistent with petroleum being the primary source, not combustion.

Plastic Debris, Toxic Chemicals, and the Food Web. PBTs are present in oceans throughout the world. Species that live in PBT-polluted water tend to concentrate the PBT from the water into their tissues—a process called bioconcentration. Predators at higher trophic levels may be directly exposed (if they live in the same PBT-polluted water), as well as exposed via PBT-tainted food. If this dual exposure occurs faster than the toxicant can be eliminated from the organism, the PBT is said to bioaccumulate. If PBTs are found at higher and higher concentrations in progressively higher trophic levels in the food web, they are said to biomagnify.

Primary Accumulation. Research on the behavior of PBTs in the guts of deposit feeders (e.g., worms that ingest sediment) showed that the surfactants present in their digestive process tend to mobilize the PBTs from contaminated sediment and make them available to the worms.[78−80] Furthermore, deposit- and suspension-feeding species ingest minute plastic particles[23] and may do so selectively over sand grains. It is possible that the digestive process also mobilizes PBTs from ingested plastic particles.

Laboratory studies suggest that mussels and other filter feeding species may ingest microplastics[81,82] during feeding and eliminate them slowly, so the particles may remain in the shellfish for weeks or months. Mussels, as well as mammals, can absorb microplastic particles into the circulatory or other organ systems.[83−85] The long residence times of these particles increase the likelihood of PBT desorption and contribute to the bioaccumulation of PBTs in the shellfish, although very long residence times may achieve equilibrium between the tissues of the organism and the plastic.[52]

As shown in Table 5, Takeuchi et al. reported a clear progression of bioconcentration and biomagnifications of PCBs in Tokyo Bay.[86] PCB concentrations increase by roughly an order of magnitude from water to shellfish and from shellfish to crabs and fish. Similar trends in PCB, DDT, and other organochlorine levels have been observed throughout the world.[87,88] Winter flounder caught near the Massachusetts shore had mean PCB levels in the 1000−6000 ppb range.[89] Even though flounder are relatively low in the food web (Figure 1, trophic level 2−3), these fish carry a substantial PCB burden, probably due to their location near a heavily industrialized region. It is not clear what the source of the PCB burden is: direct exposure, dietary exposure, or ingestion of PCB-laden plastic debris.

Table 5. Concentrations of PCBs in Surrounding Water, Filter Feeders, and Higher Trophic Levels in Tokyo Bay[86]

	reported concentration of PCBs (ppb)
water	0.93−1.02
mollusks	23.3−73
crabs and fish	113−367

Borga et al. found that for arctic cod, over 87% of the exposure to a specific PCB congener was through food rather than absorption directly from water.[90] Arctic cod are in the middle of the food web (Figure 1, trophic level 3−4), so it is not surprising that the majority of the burden for a PBT is from food rather than direct absorption from the water, as is common for the lowest trophic levels.

Filter feeders, deposit feeders, and small fish all ingest plastic[23,31,33,91,92] and, to the extent that that plastic is tainted with PBTs, may increase their body burden of PBTs relative to directly absorbing the PBTs from the water column (bioconcentration) or their natural diet (bioaccumulation). Thermodynamic modeling of partitioning PBTs between air, water, natural organic carbon, and polyethylene suggests that ingested PE may be a small, if not negligible source of PBTs for marine species.[52] However, this thermodynamic model may significantly underestimate the amount of PBTs transferred from plastic to the ingesting organism because surfactants in the gut change the kinetic and equilibrium behavior of PBTs. Additional research is required to better understand both the kinetic and thermodynamic behavior of PBTs partitioning between plastic and ingesting organisms.

Adding tainted plastic to the diet at any trophic level may significantly increase the amount of PBTs available to the food web, especially given the relatively high concentration of PBTs in plastic (Table 4) compared to species near the bottom of the food web (Table 5). Even when considering different absorption rates when a predator eats tainted plastic or tainted prey, plastic debris could act to concentrate PBTs from the water column to the food web. Whatever the source, PBTs are present in most marine species, although the exact concentration and distribution of PBTs depend on a combination of the toxicants present.

Accumulation in Higher Organisms. Unlike the low-trophic-level fish and invertebrates, sea birds do not directly absorb significant amounts of PBTs from the environment—they simply are not continually exposed the way marine organisms are while immersed in water. On the other hand, sea birds do have significant exposure through their diets, both from the tainted food in the food web and from ingesting tainted plastic. Years of research have documented plastic ingestion by seabirds and the potential to transfer PBTs from ingested plastic.[51,76,93−96] In a study of preen gland oil of 30 specimens across 13 species, Yamashita et al. found PCBs ranging from 43 to over 10 000 ppb.[97] Gurunge and Tanaka found that open-ocean predatory birds had PCB levels similar to near-shore birds concluding "that unknown factors like trophic status and non-point pollutant sources... are yet to be resolved".[98] This may be evidence that PCBs that were sorbed to plastic and dispersed globally are a significant source of PCBs in the food web.

Probably the most concerning research was performed by Teuten at al. examining streaked shearwater chicks[29] using preen gland oil to monitor body burden, a noninvasive method developed by Yamashita et al.[97] Researchers added a single dose of about 1 g of plastic collected from Tokyo Bay that contained an average of 100 ng of PCBs (not an unusual amount, as shown in Table 4) to a daily diet of 10−120 g of fish that contained an average of 15 ng of PCBs. Chicks fed the plastic showed increased body burden on the order of 25−100%.[29] That a single dose of plastic, amounting to only 1−10% by weight of the birds' diet on that day can lead to such a significant increase in PCB body burden is very concerning. While the total PCB load from that 1 g of plastic is about 6 times greater than the daily PCB load from the fish diet, it is surprising how efficiently the PCBs desorb from the indigestible plastic in the chick's gut. This clearly demonstrates that even small amounts of tainted plastic can substantially increase body burden of PBTs when plastic is ingested.

Spikes in PCB burden upon feeding plastic debris to birds conflict with a fugacity model published by Gouin et al. that predicts decreases in body burden of PBTs from ingestion of polyethylene.[52] Soon-to-be published results from Rochman et al. measuring body burden of PBTs from tainted plastic fed to medaka[99] may shed additional light on the kinetic and thermodynamic behavior of the mobility of PBTs from ingested plastic. The difference may be entirely attributable to kinetic effects in that plastic debris may not remain in the organism long enough to achieve equilibrium. Gouin's model also neglects any role of digestive enzymes that may mobilize chemicals from the surface of the debris.

Exactly how much burden of PCBs and other PBTs present in the many species that ingest plastic is attributable to this

mechanism is not clear. Given the widespread evidence of plastic ingestion by many species and that PBTs can desorb in the gut of a variety of animals that eat tainted plastic, it is possible that a substantial portion of the PBTs present at any trophic level (green wedge in Figure 1) is there because either that animal or its prey eats tainted plastic, although there will be wide variability in the body burden due to this mechanism. It certainly should not be surprising to find some PBT contribution in any organism that ingests plastic.

Like seabirds, sea turtles generally have significant concentrations of PBTs present in their tissues[100−103] and eggs.[104−106] Also like seabirds, sea turtles ingest plastic debris[107−110] as well as prey tainted with PBTs. As a result, sea turtles are at risk from PBTs in the water column, their prey, and sorbed by plastic debris.

Marine mammals can be sentinel species to understand the transfer of toxics to the top of the food chain. Research on plastic particle sizes in seal scat suggests that seals do not directly ingest plastic.[31] Instead, the seals eat fish that have, in turn, eaten small plastic particles in a "plastics concentrating stage". That is, the fish selectively eat the small pieces of plastic, and then the seals eat the contaminated fish.[31] This confirms work by Carpenter et al.[75] Because seals eat dozens or hundreds of fish, plastic particles are hundreds of times more concentrated in seals than in fish. The seals consume both the fish tainted with toxic chemicals as well as the plastic consumed by the fish. Seals have been found with PCB concentrations in their fat tissues as high as 1370 ppb.[111] A range of top-level predator marine mammals have been found with PCB concentrations between 1 ppm (1000 ppb) in seals and nearly 1000 ppm in orcas.[112] PCB concentration in common dolphins was found to range from 200 to 6200 ppb.[113] The amount of these PCB levels that is attributable to plastic marine debris is unknown. While humans do not exclusively consume seafood as marine mammals do, our seafood does contain a variety of PBTs and plastic may increase the burden of persistent, bioaccumulative, toxic chemicals, to some as yet unknown degree.

Human Body Burden of PBTs. The fact that PBTs are present in human diet is well documented (for an example, see Kirk-Othmer Encyclopedia of Chemical Technology[114]). The National Health and Nutrition Examination Survey (NHANES) data tracks a variety of PBTs, including PCBs. Jain and Wang use 2001−2002 NHANES data to calculate a geometric mean (lipid-adjusted) concentration of the PCBs in humans as 103.6 ppb.[115] While there are a variety of sources of PCB exposure,[116] diet continues to be the dominant source of PCB body burden.

Among other indicators (such as age and body mass index), dietary intake of fish and shellfish are predictors of serum concentrations of PBTs in pregnant women.[117] Furthermore, in Japan, mean daily intake of dioxins and dioxin-like compounds, including PCBs, was highest from consuming fish and shellfish, accounting for about 54% of the total "toxic equivalents" (TEQ) of dioxin and dioxin-like compounds consumed.[118] PCBs in fish and shellfish accounted for a mean of 57 ± 41 pg TEQ/person/day (of a total 68 ± 56 pg TEQ of PCBs/person/day). This equates to PCBs in fish and shellfish being responsible for nearly 35% of the total daily burden of dioxins and dioxin-like compounds[118] in the Japanese diet (161 pg TEQ/person/day or 3.22 pg TEQ/kg body weight/day).

In the U.S., fish (especially freshwater) had the highest levels of PCBs, dioxins, and dioxin-like compounds of all food categories, but daily intake of fish is lower than that in other countries, accounting for less than 10% of the total intake of PCBs.[119] For example, U.S. men, age 20−79, ingest about 171 pg TEQ/day. Of that, about 14.5 pg/day is due to fish ingestion. This accounts for about 0.2 TEQ pg/kg body weight/day of the total intake of 2.4 pg TEQ/kg body weight/day.[119]

While there is no firmly established tolerable daily intake (TDI), the World Health Organization estimates a TDI of 1−4 pg TEQ/kg body weight/day.[120] The European Union has established a tolerable weekly intake of 14 pg/kg body weight,[121] the equivalent of a 2 pg/kg body weight/day. In both U.S. and Japan, the total TEQ burdens (2.4 and 3.22 TEQ/kg body weight/day) fall within the 1−4 pg TEQ/kg body weight/day range, so there is some concern for toxicity from PCBs at current levels of PCBs and plastic debris polluting the ocean. There is no "room" for additional PCB burden.

In summary, plastic marine debris is only a temporary sink for PBT substances. Rather than removing PBTs from the ocean, plastic appears to transfer a nonzero amount of PBTs from the water column into marine species. While current research cannot quantify the amount, plastic in the ocean does appear to contribute to PBTs in human diet.

PLASTIC DEBRIS AS A SOURCE OF TOXIC CHEMICALS

Plastics are often a mixture of a polymer (such as those listed in Table 2) and a variety of components that enhance performance, including plasticizers that make the plastic soft or pliable, and antioxidants and other stabilizers that prevent degradation of the plastic. Chemicals that may leach from plastic in the ocean include phthalates from PVC, nonylphenol compounds from polyolefins, brominated flame retardants (BFRs) from ABS or urethane foam, and bisphenol A (BPA) from polycarbonate.

Leaching predominantly occurs at the plastic's surface. The plastic surface is then depleted of plasticizer until more plasticizer diffuses to the surface or the plastic fragments into smaller pieces, exposing new surfaces. Through this slow process of leaching and fragmenting, plastics may be a long-term source of toxic chemicals despite the fact that many of these chemicals break down in a matter of weeks to months.

Phthalates. Phthalates are a class of chemicals most commonly used to make rigid plastics soft and pliable. PVC, also called vinyl, is a tough, rigid plastic often used in construction as drain pipes, vinyl siding, or vinyl frames for windows. However, with the addition of 30% (by weight) of plasticizers,[123] the PVC becomes soft and pliable enough to use as a shower curtain, medical tubing, or a child's teething toy. Phthalates generally do not persist in the environment over the long-term,[124] but there is evidence that environmental concentrations are above concern thresholds in some aquatic environments.[125]

Phthalates may leach from plastic debris on a fairly steady basis.[126−128] Phthalates have fairly low bioconcentration factors,[124] so the human body burdens reported by Oehlmann et al.[125] are likely due to a variety of exposures other than just fish ingestion,[124,129] including drinking water or direct exposure to plasticized vinyl products.

Nonylphenol. Nonylphenol (NP) is the intermediate degradation product of the widely used nonylphenol ethoxylate (NPEO) class of surfactants and some antioxidants (preserva-

tives), such as tris(4-nonylphenyl) phosphite (TNPP). The parent compounds (NPEO and TNPP) are fairly susceptible to microbial degradation, but nonylphenol itself persists for months.[130−132] NP is present in plastic debris both as the parent NPEO and TNPP and from resorbtion of NP from seawater.[46] NP does not seem to biomagnify up the food chain.[46,86,133,134] However, NP concentration in human breast milk does correlate positively with fish ingestion,[135] providing evidence that NP does accumulate in fish.[134,136] NP is toxic to mammals and very toxic to aquatic species.[130] Furthermore, there is significant uncertainty about endocrine disruption effects of NP which may operate at much lower concentrations than the toxicity threshold established for NP. Mato et al. measured concentrations of NP in polypropylene pellets up to 16 000 parts per billion (by weight), however, this level seems largely due to NP present in the plastic rather than sorbtion of NP from the environment.[46,51] High levels of NP in plastic debris and the fact that NP does not accumulate in marine species suggests that ingestion of plastic debris may be a significant source of NP for marine species.[51] Given that the concentration of concern for aquatic toxicity is as low as 0.7 parts per billion in water,[130] NP leaching from plastic marine debris probably contributes to risk for fish populations. Undegraded NPEO and TNPP may also adversely effect fish. On the other hand, unless its endocrine disrupting effects are very much lower than the established no-effect level for humans, it is not clear that NP from plastic debris is a risk for human health.

Bisphenol A. Bisphenol A (BPA) is primarily used as a monomer to make polycarbonate plastics (shatter-proof glass, CDs, and DVDs) and epoxy coatings (e.g., lining the insides of cans). It is also used in thermal printing paper.[137] Residual BPA can leach from either polycarbonate plastics or epoxy coatings. There is evidence that leachate from landfills may be a significant source of BPA in the environment.[29,138] BPA is moderately biodegradable, generally degrading faster after microorganisms become acclimated.[139,140] Degradation in seawater is much slower than fresh water.[140,141] Despite its degradability, BPA does accumulate in fish[136,142] at concentrations higher than observed concentrations in canned foods[143] (thought to be one of the primary sources of human exposure). Depending on an individual's relative rates of fish ingestion and ingestion of canned food, BPA in fish tissue may be the primary source for dietary BPA.[143]

Plastic debris may be an important source of phenols (e.g., nonylphenol and BPA) relative to tissue concentration in prey species because of phenols' low bioconcentration and bioaccumulation potentials.[29] That is to say, unlike other PBTs, phenols do not strongly concentrate in fish tissue without the presence of plastic debris in the fishes' diet. This is especially true for BPA because of its short environmental lifetime.[137] Given that BPA concentrations have been measured in plastic debris up to nearly 300 ppb,[29] plastic debris may be the major source of BPA in seafood,[143] but further research would be required to confirm and quantify the contribution of plastic to BPA body burden in fish.

Acceptable human exposure levels of BPA are still open to question,[137,144,145] however, an expert panel concluded that "human exposure to BPA is within the range that is predicted to [have some biological effect, including toxic effects] in over 95% of people sampled".[146]

Brominated Flame Retardants. Flame retardants are added to plastics to reduce their flammability and lengthen the time available for people to escape fires. Flame retardants may simply be mixed in (as is the case with polyurethane foams) or they may be reacted to become part of the polymer (as with some epoxy resins and some polystyrenes). The greatest concerns are for the brominated flame retardants (BFRs) that are mixed into plastic resins since they are more available to leach out of the plastic. BFRs include polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and brominated polystyrene.[144,147]

Polybrominated diphenyl ethers (PBDEs) are highly persistent, bioaccumulate, and are of particular concern for children's health.[148] While household exposures (e.g., dust) are a significant contributor to children's burden of PBDEs, food and breast milk may be the dominant source.

Tetrabromobisphenol A (TBBPA) is both reacted into plastic—it is a monomer used to make the polymer—and it is added to plastics to reduce flammability without becoming part of the polymer. In marine sediment where there is little or no oxygen, TBBBPA can degrade to and persist as Bisphenol A.[149]

In the marine environment BFRs may leach directly from plastics, such as ABS, a plastic employed for many uses including outer casing for electronics, or be transported from land-based sources—PBDEs have significant long-range transport potential.[150] PBDEs do bioconcentrate and biomagnify, but less so than PCBs.[151] PBDEs have been found in a variety of foods, including fish.[89,152−154] A variety of marine mammals were found with PBDE concentrations ranging from 0.42 to 4950 ppb with a average concentration of 793 ppb.[155]

In humans, it is not clear whether PDBE levels in breast milk and blood correlate with dietary intake: some studies suggest such a correlation,[152,154,156] others show no correlation.[152,153,157,158] Recent work suggests that ingestion of or dermal contact with household dust accounts for the vast majority of PDBE body burden.[158−162] This is not surprising given how many household items contain PDBEs as flame retardants. After household dust, studies suggest that the greatest source of PBDEs in the diet is seafood (shellfish and fin fish).[161,163] Other research indicates that meat and poultry drive dietary exposure to PDBEs.[159] The observed variability in PDBE body burden suggests that there are multiple, significant exposure pathways, including fish ingestion.

Even with immediate phase-out of BFRs, sufficient quantities are present in durable goods that have already been purchased to provide for steady, disperse release to the environment over the coming years. A complete and immediate phase-out of commercial use of BFRs would shift the main exposure from indoor exposures to exposures through the food supply, but would not eliminate exposure to BFRs for many years.[164,165] In any case, plastic marine debris would be a sink for BFRs (like other PBTs) as well as a source.

Plastics and Toxics—Summary. There is a synergistic effect between two common ocean pollutants: persistent, bioaccumulative, toxic chemicals (PBTs) and plastic debris. Plastic serves to concentrate and transfer toxic chemicals from the ocean into the marine food web and to human diets. While it is not currently possible to accurately calculate how much of the toxic chemical load present in human diet is attributable to this mechanism, the fact that plastic and toxics interact in this way increases the risk to humans and wildlife. Research on the extent and nature of this synergy is ongoing and will continue to provide insight into the magnitude of the problem.

Plastic debris is also a source for toxic chemicals in the ocean. Currently plastics contain a range of toxic substances, some of

which are persistent and bioaccumulative (e.g., brominated flame retardants), others less so (e.g., bisphenol A). For the less persistent, bioaccumulative substances, it is not clear how much enters the food web and if they impact on human health.

While further research on the extent to which plastic debris transfers toxics to the marine food web will help inform risk assessment, such information will simply add urgency to the existing problems associated with plastic marine debris. Because of the disperse nature of both toxics and plastics in the ocean, prevention strategies are critically important to reducing both plastic debris and concentrations of toxic chemicals.

POTENTIAL SOLUTIONS

Policy Challenges. Among the challenges in addressing marine debris is that the greatest impacts are largely invisible from the origin of the debris (fugitive loss, litter, or other improper disposal). Someone who accidently drops a plastic wrapper while walking in the park is unlikely to see the damage done when that wrapper reaches the ocean.

Another significant challenge is that marine debris arises from sources around the world. Unilateral action by the United States will be helpful, but cannot, by itself, solve the problems presented by marine debris. Debris dropped anywhere on earth may end up being transported via surface water to the ocean where it may be carried vast distances[15,73] before it settles to the bottom.[4]

Furthermore, plastic debris is simply too widely dispersed to effectively clean it up. Even in the "Great Pacific Garbage Patch" there are only a few kilograms of plastic per square kilometer of ocean.[9,17] This is roughly equivalent of a few teaspoons of plastic pieces spread over a football field and trying to clean it all up with tweezers. Reversing the impacts of plastic debris will take sustained efforts and novel technologies.

By far the best solution to plastic marine debris is to prevent the debris from entering the water system, either land-based debris (e.g., litter, fugitive releases from trash handling and landfills, etc.) washed into surface water or blown out to sea, or ocean-based (e.g., trash from ships or platforms, or derelict fishing gear).[166] Efforts by a wide variety of organizations, including the U.S. EPA, National Oceanic and Atmospheric Administration, the United Nations Environment Programme, Intergovernmental Oceanographic Commission, and Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP), as well as non-governmental organizations such as Algalita Marine Research Foundation, Surfrider Foundation, among others, have raised awareness of problems associated with marine debris and are due credit for the leveling off of the abundance of marine debris.[4,9,20,21]

Prevention. Plastics are extraordinarily useful for a wide variety of uses, but for many plastic items, their durability far exceeds their service life. Reduced reliance on single-use plastic items, such as bags, beverage bottles, and food service ware, and increased recycling of plastic will conserve fossil resources, reduce landfill burden, and help reduce the likelihood that plastic items become marine debris.

However, even with effective prevention strategies, some plastic will inevitably find its way to the ocean. How can the impact of this fugitive plastic be minimized? A commonly suggested solution is degradable plastics but this immediately begs the question as to what is meant by "degradable".[2,8,167] Degradation may mean embrittlement to prevent entanglement or it may mean the ultimate degradation to CO_2 and water (also called mineralization).[3,167−170] Embrittlement leads to fragmentation. Fragmentation reduces many of the most visible impacts (entanglement, stranding), but it increases the concentration of microdebris and the concomitant impacts on the food web.

Even the total mineralization of plastic is not entirely benign. Doering et al. reported that the degradation of a variety of biodegradable polymers reduces the availability of nitrogen nutrients normally released from the sea floor.[171] Biodegradable plastic may interfere with native flora receiving nitrogen nutrients. Keeping plastic out of the oceans is the best option; on the other hand, biodegradation is preferable to the accumulation of persistent plastic debris.

Biodegradable Plastics. There are a range of biodegradable plastics, many of which are also biobased (produced from annually renewable biomass). These plastics are making inroads to a variety of plastic markets. In most cases, their market success is attributable to their functional properties and cost, not their degradability. In other cases, their degradability is the key property that drives their selection. For example, coastal restoration efforts in the Chesapeake Bay include planting dune grass to retard the erosion of sand dunes. Dune grass is planted in a plastic stake to provide stability while it takes root. In years past PVC was used. The PVC would eventually fracture and become persistent debris. Recent planting has used a polyhydroxyalkanoate (PHA) plastic instead of PVC.[172]

It is important to note that not all bioplastics are biodegradable and not all biodegradable plastics are biobased. In many cases, biodegradable plastic may be a drop-in replacement for traditional plastic. Their properties may prevent biobased plastics from being used in some applications, especially high-performance ones. On the other hand, the properties of the new plastic may allow new uses. Table 6 shows three commercial biodegradable plastics, some resins each may substitute for, and a number of potential uses.[173−175] Note that PLA is listed here, but does not formally meet the definition of biodegradability. However, it is compostable in commercial composting facilities and is much more likely to degrade in a marine environment than PET, polyolefins, or polystyrene.

Table 6. Examples of Biodegradable Polymers, Traditional Polymers They May Replace, and Some Potential Uses

polymer	may replace	potential uses
starch blends/modified starch	PET, PE, PP, PS	packaging, medical products, food service items
PHAs, including polyhydroxybutyrate and polyhydroxyvalerate	PP, PS, PVC, ABS, PC	food service items, durable goods, packing, coastal restoration
PLA	PET, PE, PP, PS	bottles, paper coating, produce containers, apparel

There may be significant opportunities for market segments that may have a substantial impact on reducing marine debris. For example, over 27% of the items recovered between 2001 and 2006 by the National Marine Debris Monitoring Program were plastic straws.[15] Straws (usually PP) and other disposable food service items (often PP, PE, or PS) are relatively low-performance applications. A voluntary program where cruise ships or waterfront hotels and restaurants receive recognition for replacing traditional plastic disposable service items with biodegradable alternatives could significantly reduce the amount of persistent plastic debris. Voluntary efforts such as

this could help biodegradable plastics to cross from being a niche to a significant portion of market and, by reaching economies of scale, better compete with the mature, traditional plastics. The benefits could then spread to other applications and other business sectors.

Another potential solution is the use of additives that increase the biodegradability of plastic. One example is an additive that enables traditional plastics to be consumed by microbes in the environment.[176] Plastics that degrade in anaerobic environments do raise concerns for the impacts from natural gas (especially methane) that will be produced in landfills. Climate change impacts from landfill gas can be minimized by recycling or by capturing the gas.

It is important to recognize that biodegradable plastics are not a panacea. There may be many opportunities to replace traditional plastics with biodegradable alternatives, but there are also many applications where degradable plastics are not an option. Manufacturers that use plastics should carefully consider how that plastic can and will be used and what will happened to it at the end of its useful life.

Reduce, Reuse, Recycle. Some may criticize biodegradable plastics as the wrong solution: the risks from landfill methane production may be too great to justify the use of biodegradable plastics to reduce risk from marine debris or biodegradable options may make consumers more cavalier about littering rather than recycling or other proper disposal.[167] Instead marine debris policy should focus on "reduce, reuse, recycle". There is no doubt that reducing plastic use, reusing plastic items, and recycling used plastic items are the best options. It is certainly better to employ a reusable shopping tote than to use a single-use bag, even a biodegradable one. They reduce the amount of virgin plastic needed and thereby save energy and materials. Another option is extended producer responsibility, which can incentivize manufactures to find ways to get their plastic back, closing the loop on resin. However, in applications where reuse and recycling are rarities, such as beverage straws, biodegradable plastics can help minimize the impact of any items that do end up in waterways.

There are some independent, market-based efforts to recover plastic material and manufacture and sell goods. Terracycle is a small company that collects plastic "trash", mostly plastic packaging, including candy wrappers, juice pouches, snack chip bags, and many others, and converts them into plastic products, such as shopping bags, kites, and many other durable goods. Terracycle uses a novel mechanism of paying for empty, branded packing, and employs consumers to collect and send the waste to Terracycle. Unlike traditional recycling, this provides highly segregated waste allowing Terracycle to better control the quality of its feedstock. The more opportunities there are to use waste plastic in profitable ways, the more plastic will be reused and recycled.

Waste-to-Energy. Others are finding ways to use unsegregated waste plastic. Covanta Energy incinerates derelict fishing gear that is brought to shore at ports around the country, generating electricity. Of course, incineration of any material can generate problematic emissions, including dioxins and furans, CO_2, NO_x, and ash. These emissions must be properly managed so as not to simply transfer the risk from the marine environment to the atmosphere. Other companies, such as QinetiQ[177] and Envion[178] convert a broad range of plastic to fuels through pyrolysis. These fuels can be used directly or blended with fossil fuels in a range of applications. Even with these options, reusing and recycling plastic are still the best options, but for plastic that cannot be recycled, waste-to-energy or waste-to-fuels may be attractive alternatives to sending plastic to landfills. A full enumeration of these options is beyond the scope of this review and merits significant research in its own right.

No Single Solution—Many Opportunities. Overall, there is no single solution to the risk posed by plastic marine debris and toxic chemicals in the ocean. While there are limited, if any, viable options to clean up plastics or toxics already present in the oceans, there are many opportunities to prevent more plastics and toxics from being released.

Plastic reduction strategies will have to include low-tech solutions to reduce littering, such as behavior change, and high-tech solutions, such as new, biodegradable resins, as well as public policy options. Public policies may include limiting trash in water discharges by, for example, physical trapping debris before discharging effluent to surface water, financial incentives to increase reuse or recycling, such as plastic bag fees, or even incentives for ambitious system-wide redesign of plastic manufacturing−use−disposal cycles to "close the loop" for resins.

Reductions in toxic chemicals will also require a range of actions. Toxic chemicals leaching from plastic can be reduced by limiting the plastic released and by substituting green chemistry technologies. New plastics that do not require additives or next-generation, green additives that do not adversely impact human health or the environment can be part of the solution. Furthermore, updating standards for flame retardancy[165] can help avoid conflicts between fire safety and public health goals. Innovative pesticides and integrated pest management strategies can both reduce the release of PBT pesticides. Finally, for PBT chemicals that cannot be reduced by process or product redesign, such as some incineration byproducts, emission limits can help keep the PBTs out of the environment.

Whatever strategies are adopted, international cooperation will be critical in limiting the risk to the oceans and the risk to humans from eating seafood. Plastic and toxics in the ocean contribute to environmental and human health risk irrespective of where the pollutants originate; it is truly a global issue.

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Notes

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■ NOTE ADDED AFTER ASAP PUBLICATION

The discussion of the study by Rochman et al. measuring body burden of PBTs from tainted plastic fed to medaka was changed to better reflect the findings of the Rochman et al. work. The correct version published on 11/7/2012.